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AB INITIO STUDY OF PHOSPHORESCENCE OF HETERO[8]CIRCULENES

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Quantum chemical calculations of phosphorescence lifetime are performed for the first time by ab initio CC2 and TD-DFT methods for hetero[8]circulenes bearing Si *and* Ge *atoms. According to the results of calculations, a lower value of* τ_{phos} *for tetragermatetrathia[8]circulene (II) originates from two factors: almost 29 times more distorted main macrocycle II and almost four times larger spin-orbit coupling matrix element between* T_1 *and* S_0 *by virtue of heavier* Ge *atoms as compared to* Si*. The* τ_{phos} *values calculated by CC2 ideally agree with its experimental value; the difference is less than 2 and 0.3 s for tetrasilatetrathia[8]circulene (I) and tetragermatetrathia[8]circulene (II) molecules, respectively. The agreement of the lifetimes calculated by TD-DFT is only within an order of magnitude. The main intramolecular decay channel of the* T_1 *state is internal conversion between* T_1 *and* S_0 *owing to simultaneous spin-orbit and nonadiabatic interaction of their wavefunctions.*

Keywords: circulenes, hetero[8]circulenes, oxygen, quantum chemistry, photodynamic therapy, phosphorescence.

INTRODUCTION

Hetero[8]circulenes are macroheterocyclic compounds with general structure shown in Figure 1*a*. The inner cycle consisting of eight carbon atoms is called the hub cycle, and the outer part of the molecule, including four heteroatoms, is called the rim cycle [1]. Hetero[8]circulene molecules have rather exotic electronic structure, which gives rise to their nonaromatic structure. It was shown in [2, 3] that the outer (rim) cycle is aromatic, and the inner (hub) cycle is antiaromatic. The degree of delocalization of the π electron density in both cycles is approximately the same, and this is why hetero[8]circulenes are nonaromatic systems.

Owing to their unique electronic and structural properties, hetero[8]circulene molecules are thermodynamically and chemically stable compounds [1]. Due to this fact, at present they are promising for different nanophotonics applications, mostly as active media of organic light-emitting diodes and transistors [1]. Until recently (up to 2017), only fluorescence of hetero[8]circulenes was studied by experiments, because the quantum yield into triplet electronic states in these compounds is negligibly low [4]. Only at the end of 2018, hetero[8]circulenes exhibiting very weak phosphorescence were synthesized [5]. These compounds bear heteroatoms of germanium and silicon (Figure 1*b* and *c*). In this case, four benzene rings are annulated in the structure for four thiophene rings. The structure of these compounds, tetrasilatetrathia[8]circulene (I) and tetragermatetrathia[8]circulene (II), is shown in Fig. 2. For these compounds, phosphorescence quantum yield (φ_{phos}), triplet electronic state quantum yield (φ_{ISC}), and lifetimes of the first excited triplet (T_1) and first excited singlet (S_1) electronic states were measured in [5]. Assuming that only T_1 lies

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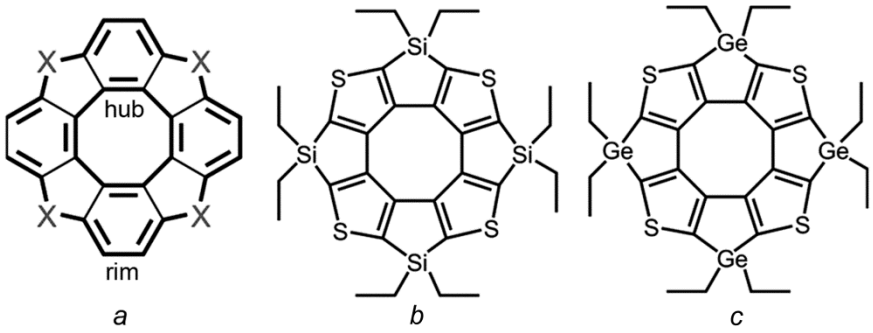

Fig. 1. General structural formula of hetero[8]circulenes (X is the heteroatom) (*a*) and circulenes studied in this work (*b* and *c*).

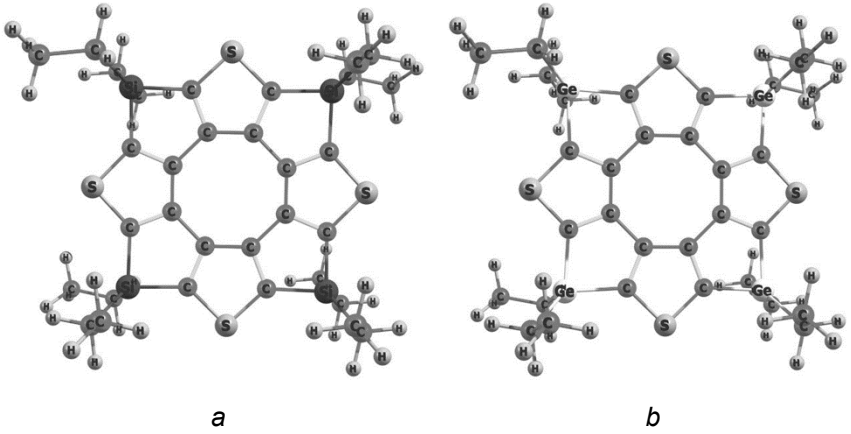

Fig. 2. The structure of tetrasilatetrathia[8]circulene (I) (*a*) and tetragermatetrathia[8]circulene (II) (*b*).

below S_1 and all other triplet excited states lie higher, Akahori *et al*. [5] estimated the rate constants of internal conversion (k_{IC}) and intersystem crossing (k_{ISC}).

The experimental measurements show that molecules I and II can be used as photosensitizers in photodynamic therapy due to their noticeable triplet quantum yield and low toxicity [5]. Therefore, understanding of the phosphorescence process in these molecules and their T_1 state relaxation as a whole is important for the development of efficient photodynamic technology based on these compounds. In addition, this suggests that such molecules can be used in the design of organic light-emitting diodes (OLEDs) as well, because triplet excitons can be efficiently utilized in electroluminescence owing to possible strong spin-orbit coupling between the ground singlet (S_0) and T_1 electronic states. Quantum chemical simulation of phosphorescence of the molecules under study can provide the necessary knowledge. Note that until now, the phosphorescence of these molecules has not yet been studied by quantum chemistry methods. Therefore, the goal of this paper is the study of phosphorescence of molecules I and II by modern *ab initio* quantum chemistry methods.

COMPUTATIONAL DETAILS

Since phosphorescence emission proceeds from the T_1 electronic state, one should obtain its optimized geometry to study the phosphorescence process. Density functional theory (DFT) with B3LYP exchange-correlation

TABLE 1. Energies of Electronic States of Hetero[8]circulene Molecule, cm^{-1}

Compound	Energy T_1, eV		
	Method		
	TD-DFT	CC2	Exp.*
I	1.72	2.28	2.26
II	2.13	2.32	2.38
	Phosphorescence lifetime τ_{phos}, s		
	Method		
	TD-DTF	CC2	Exp.*
I	130	33	31
II	34	1.5	1.2

*Note. The experimental data are from [5].

functional [6] and 6-31G(d, p) basis set was used for geometry optimization of I and II in the T_1 electronic state. The same 6-31G(d, p) basis set and B3LYP functional were also used in other calculations by DFT and its time-dependent version (TD-DFT) [6].

To calculate the energy of the T_1 electronic state in the T_1 geometry of molecules I and II, we used TD-DFT [6] and approximate second-order coupled cluster method (CC2) [7, 8]. To calculate the radiative, or phosphorescence, lifetime (τ_{phos}) of the T_1 state of I and II, we used quadratic response theory in which perturbation operators were the spin-orbit coupling operator mixing the triplet and singlet wavefunctions and the operator of interaction of the molecule with an external electromagnetic field [9]. Note that quadratic response theory for the phosphorescence lifetime was implemented in the DALTON program package [10] in the 1990s at the TD-DFT level [9], while its *ab initio* level (CC2) [11] was implemented only in 2015 in the TURBOMOLE program package [12]. Therefore, calculations at the TD-DFT level were performed by DALTON, and the calculations at the RI-CC2 level were performed by TURBOMOLE on the supercomputer SKIF Cyberia of Tomsk State University. The calculations by CC2 utilized def2-TZVP basis set.

RESULTS AND DISCUSSION

1. Equilibrium geometries of the T_1 electronic state of molecules I and II

The optimized equilibrium geometries of the T_1 electronic state of molecules I and II are nonplanar. This sets them apart from the prototypical hetero[8]circulene, tetraoxa[8]circulene [4], whose macrocycle is planar and has D_{4h} symmetry [4]. Therefore, the D_{4h} symmetry in molecules I and II is only approximate. Four sulphur atoms in the thiophenes of molecule I make a dihedral angle of 0.009°, while in molecule II they make a dihedral angle of 0.26°. Therefore, molecule II is nonplanar to a greater extent than molecule I. This effect leads to that the angular momentum selection rules in the D_{4h} symmetry group, typical for tetraoxa[8]circulene molecule, are inapplicable for molecules I and II. The nonplanar geometries of I and II result in nonzero spin-orbit coupling matrix elements between T_1 and excited singlet electronic states, which are zero in tetraoxa[8]circulene. Therefore, the phosphorescence in molecules I and II can be observed, because it is governed by spin-orbit interaction [5]. In tetraoxa[8]circulene, it is absent due to zero spin-orbit coupling matrix elements between these states [4].

2. Energy and radiative lifetime of the T_1 state of molecules I and II

The calculated energy of the T_1 electronic state and its radiative lifetime are given in Table 1. One can see that CC2 method shows a very good agreement of the calculated T_1 energy with its experimental value; the deviation is no more than 0.02–0.06 eV or 161–484 cm^{-1} for both molecules. Note that usually the electronic energies are calculated by

ab initio methods to within 0.1 eV [13]. On the other hand, TD-DFT exhibits larger deviation of the T_1 energy from the experimental data; the error is 0.25–0.54 eV. This error of TD-DFT is most likely due to an incomplete account for the exchange-correlation effects and can be eliminated by the choice of a functional with proper nonlocal exchange term [6]. Note that the experimental T_1 energies are accurate to within 1 nm or 0.004 eV [4].

According to Table 1, the phosphorescence lifetime calculated by CC2 is in a very good agreement with the experimental data, since the difference is 2 and 0.3 s for molecules I and II, respectively. Note that usually, τ_{phos} calculated by TD-DFT agrees with the experimental value within an order of magnitude [9], and the experiment was accurate to within 10% [5]. Therefore, the deviation of τ_{phos} for molecules I and II calculated by TD-DFT to within an order of magnitude is not anomalous. A possible reason for the greater error in the τ_{phos} calculated by TD-DFT as compared to CC2 is the greater error in the calculated T_1 energy.

According to Table 1, the lifetime τ_{phos} of compound II is 22 (CC2) or 26 (experiment) times shorter than that of compound I. First, this effect originates from the fact that macrocycle II is less planar than I, which results in stronger violation of the angular momentum selection rules in the D_{4h} symmetry group and therefore in the increased spin-orbit coupling. Second, the internal heavy atom effect of Ge (as compared to Si) manifests itself through the Z^4 dependence of the spin-orbit coupling on the atomic nuclear charge Z [14, 15]. Indeed, CC2 calculations show that one-electron spin-orbit coupling matrix elements between T_1 and S_0 differ approximately four times (1.9 cm^{-1} for germanium-containing circulene and 0.53 cm^{-1} for silicon-containing one). Under assumption that the main promoting vibrational mode for intersystem crossing has a frequency of 1400 cm^{-1}, one can use formula [4]

$$k_{ISC} = 1.6 \cdot 10^9 <\varphi(T_1)|H_{SO}|\varphi(S_0)>^2 F_{0n},$$

where $<\varphi(T_1)|H_{SO}|\varphi(S_0)>$ is the spin-orbit coupling matrix element under consideration, $F_{0n} = y^n \exp(-y)/n!$, y is the Huang–Rhys factor equal to 0.3 in this case, $n \approx E(T_1)/1400$, and $E(T_1)$ is the energy of the triplet electronic state, in cm^{-1}. With these values, one can obtain the following k_{ISC} between T_1 and S_0: $8.5 \cdot 10^{-9}$ s^{-1} for I and $2.3 \cdot 10^{-9}$ s^{-1} for II. According to the experimental measurements of [5], the phosphorescence quantum yield of I is 0.0075, and the same value of II is 0.084; the total lifetime T_1 of I is 235 ms, and the same value of II is 98 ms. Using the experimental value of φ_{phos} and the calculated k_{ISC} and τ_{phos} values, one can estimate the internal conversion rate constant k_{IC} between the spin-mixed states T_1 and S_0 using the known formula $1/\tau = 1/\tau_{phos} + k_{ISC} + k_{IC}$, where τ is the experimental total lifetime of T_1 [13]. According to our estimates, k_{IC} is 4.2 s^{-1} for I and 9.4 s^{-1} for II. Therefore, the calculations show that the main intramolecular decay channel of the excited electronic T_1 state is the internal conversion between T_1 and S_0 owing to simultaneous spin-orbit and nonadiabatic mixing of their wavefunctions.

CONCLUSIONS

In this work, quantum chemical calculations of phosphorescence lifetime of two hetero[8]circulenes have been performed for the first time by *ab initio* CC2 and TD-DFT methods. The results explained the shorter phosphorescence lifetime of molecule II as compared to I. According to our calculations, shorter τ_{phos} of II originates from two factors: almost 29 times more distorted main macrocycle of II, and almost four times higher spin-orbit coupling matrix element between T_1 and S_0. This suggests that compound II will be more efficient in photodynamic therapy than compound I. In addition, it is worth noticing that the nonplanar macrocycle of these molecules is the major cause of nonzero spin-orbit coupling matrix elements between the lowest singlet and triplet electronic states. Large nonzero spin-orbit coupling between T_1 and S_0, especially in II, is the main driving force for potential use of these compounds in OLEDs, where triplet excitons can be efficiently utilized.

Our calculations also show that the main decay channel of the excited T_1 state is the internal conversion between T_1 and S_0. Note that the internal conversion between these states is nonzero owing to simultaneous spin-orbit and nonadiabatic interaction of their wavefunctions.

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